THE VISIBLE EMISSION SPECTRUM OF BiF

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Plate V

ABSTRACT. The visible band system of BiF has been reinvestigated both under low and high dispersion. The vibrational analysis of the system has been considerably extended to include about 65 bands in the region (λ 5000–5700 Å). From a rotational analysis of four bands (2,0), (1,4), (2,5), and (3,3) the constants of the upper $v' = 2$ and 3 and lower $v'' = 4$ and 5 levels have been newly determined.

INTRODUCTION

Recently T. A. P. Rao and P. T. Rao (1962) studied the emission spectrum of BiF excited in high frequency discharge in the visible and ultraviolet regions. The well known visible system in the region (λ3600–λ5200 Å) was designad as $A-X_1$. In the ultraviolet region (λ2250–λ3200 Å), system C' reported by Rochester (1937) was observed and analysed into three systems designated as C_1-X_2, C_2-X_3 and C_3-X_1. The levels X_1, X_2 and X_3 were identified with $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$ of the ground state electron configuration

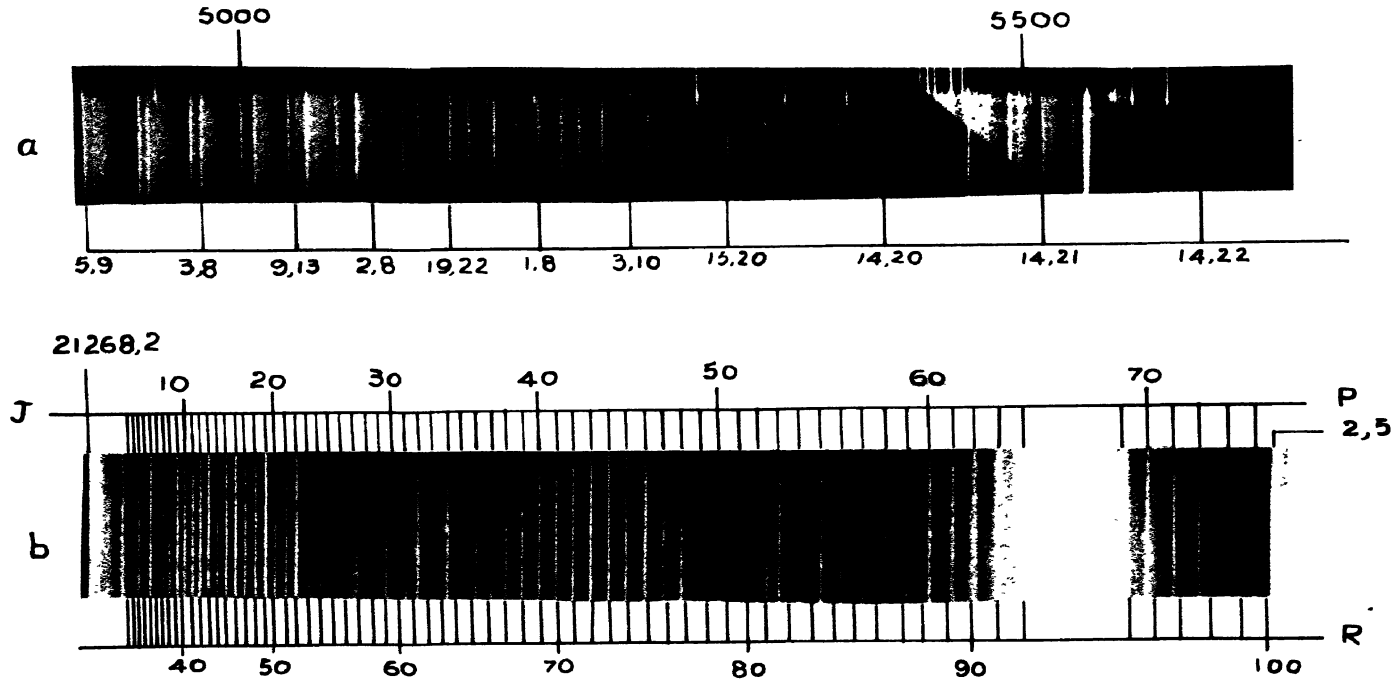
$$(z\sigma)^2\,(y\sigma)^2\,(x\sigma)^2\,(w\pi)^4\,(v\pi)^2 \ldots {}^3\Sigma^-,\ {}^1\Delta,\ {}^1\Sigma^+$$

The first excited state A was attributed to $^3\Sigma^-$ of the first excited electron configuration

$$(z\sigma)^2\,(y\sigma)^2\,(x\sigma)^2\,(w\pi)^3\,(v\pi)^3 \ldots {}^3\Sigma^-$$

From the results of a rotational analysis of five bands (1, 0), (0, 0) (0, 1), (0, 2) and (0, 3), it was shown by Rao and Rao (1962), that this system arises from a 0^+-0^+ transition which is a case (c) equivalent of $^3\Sigma^--^3\Sigma^-$. The rotational constants of the upper state A have been carried out only for the vibrational levels $v' = 0$ and 1. The rotational structure of four bands (2,0), (1,4), (2, 5) and (3, 3) has now been examined in the second order of a 21ft. grating spectrograph (dispersion 1.25 Å/mm). From a detailed rotational analysis of these bands reported below the rotational constants of $v' = 2$ and 3 of the upper state and $v'' = 4$ and 5 of the lower state have been newly determined.

The vibrational analysis of the $A-X_1$ system in the region (λ3600–5900 Å) has been considerably extended to include about 65 bands newly obtained in the present investigation.



(a) New additional bands in the visible A—X_1 system of BiF

(b) Fine structure of the (1, 4) Band of the A—X_1 system of BiF

EXPERIMENTAL

The $A-X_1$ system of BiF was easily excited in a high frequency discharge from a 500 Watt oscillator working at a frequency of 30-40 Mc/sec using specpure sample of BiF_3 taken in a conventional type of quartz discharge tube. When a characteristic bluish discharge was maintained by continuous external heating of the substance, in the visible system, new bands in the region (λ 5000-5700 Å) were observed and photographed on a Hilger three prism glass Littrow Spectrograph. About 65 bands have been measured on a Hilger comparator using iron arc standards.

Some of the bands of the $A-X_1$ system were also photographed in the 2nd order of a 21 ft. concave grating spectrograph using Agfa Isopan super special plates. The rotational structure of the four bands (2, 0), (1, 4), (2, 5) and (3, 3) was found to be free from overlapping of the neighbouring bands. The rotational lines of these bands were measured using iron arc wavelength standards. The relative accuracy in the measurement of rotational lines is about 0.07 cm^{-1}.

(a) *Vibrational analysis*

The A-X_1 system of BiF was reported by previous workers (Howell and Rochester, 1939 and Morgan, 1936) to consist of only about 40 bands in the region (λ4150-λ5100 Å). In the present experiments about 65 new bands have been obtained in the region ($\lambda5000-\lambda5700$ Å) and reproduced in plate 1(a). According to Howell the band heads of the $A-X_1$ system could be represented by the Quantum formula

$$\nu = 22959.7+381.0(v'+1/2)-3.00(v'+1/2)^2+.010(v'+1/2)^3$$
$$-510.7(v''+1/2)+2.05(v''+1/2)^2$$

A vibrational analysis of the new bands has shown that they constitute an extension of the $A-X_1$ system. The wavenumbers, classification and other data of the bands are given in Table I. About 60 bands could be classified and represented by the above quantum formula. The agreement between the observed and calculated values for most of the bands is within 4 cm^{-1} as can be seen from Table I.

(b) *Rotational analysis*

From considerations of electron configurations and electronic states in BiF, the $A-X_1$ visible system was assigned as $^3\Sigma^- - ^3\Sigma^-$. Since the rotational structure of each of the bands (1, 0), (0, 0), (0, 1), (0, 2) and (0, 3) reveals only the existance of only two branches P and R, the bands were assumed to arise from a 0^+-0^+ transition which is a case (c) equivalent of $^3\Sigma^- - ^3\Sigma^-$. The rotational structure of each of the four bands examined in the present work also reveals the presence of the two branches P and R thus confirming the above transition. The J numbering is fixed for the (2, 0) and (2, 5) bands by a comparison of the upper state combination differences. The J numbering in the (1, 4) band is fixed by

TABLE I

Assignment v' v''	Intensity	ν Obs	ν Cal	ν Obs$-\nu$ Cal
0 4	7	20894.7	20893.0	+1.7
5 8	6	20787.4	20788.2	−0.8
1 5	6	20781.5	20780.3	+1.2
6 9	6	20670.5	20670.3	+0.2
2 6	6	20665.4	20664.6	+0.8
7 10	4	20555.4	20554.3	+1.1
3 7	6	20548.0	20545 8	+2.2
8 11	4	20435.3	20440.9	−5.6
5 9	6	20315.3	20313.1	+2.2
1 6	4	20295.5	20292 2	+3.3
6 10	6	20203.9	20200.6	+3.3
2 7	5	20185.0	20179.7	+5.3
7 11	5	20095.6	20088.7	+6.9
3 8	5	20071.8	20067.9	+3.9
8 12	5	19982.9	19979.4	+3.5
4 9	5	19960 3	19955.9	+4 4
9 13	3	19874.4	19873.3	+1.1
5 10	5	19850 5	19844.7	+4.8
10 14	3	19774.6	19771 0	+3.6
6 11	5	19739.4	19734.9	+4.5
2 8	2	19707.7	19702.2	+5.5
17 20	5	19638.9	19636.4	+2.5
19 22	5	19534.1	19536.9	−2.8
20 23	4	19497.9	19501.5	−3.6
0 7	3	19430 3	19434 5	−4.2
5 11	3	19376 0	19379.1	−3.1
1 8	4	19335.8	19331.9	+3.9
6 12	4	19278.5	19273.4	+5.1
17 21	4	19216.8	19211.8	+5.0
3 10	2	19124.5	19124.4	+0.1
20 24	4	19088.3	19089.2	−0.9
13 18	3	19059 6	19056.1	+3.5
4 11	2	19025.5	19020.6	+4.9
14 19	3	18982.2	18979.1	+3.1
9 15	2	18968.5	18970.8	−2.3
0 8	2	18959.5	18956.6	+2.9
5 12	2	18918.6	18917.6	+1.0
15 20	4	18909.2	18908.9	+0.3
6 13	2	18817.1	18816.0	+1.1
11 17	2	18790.4	18787.0	+3.4

TABLE I (*contd.*)

Assignment v' v''	Intensity	ν Obs	ν Cal	ν Obs − ν Cal
7 14	3	18720.0	18716 4	+3.6
21 26	2	18664.9	18664.2	+0 7
4 12	3	18558.1	18559.1	−1 0
14 20	2	18546 2	18550.4	−4.2
5 13	3	18465 4	18460.2	+5.2
6 14	2	18366.9	18362 7	+4 2
11 18	2	18348.8	18350.1	−1.3
18 24	1	18330.7	18332 9	−2.2
2 11	3	18295.0	18293.1	+1.9
14 21	2	18125.9	18125 8	+0.1
5 14	2	18009.7	18006 9	+2 8
17 24	2	17965.1	17962.7	+2 4
1 11	1	17920.0	17922.8	−2.8
6 15	1	17910.6	17913 5	−2.9
20 27	1	17881 4	17876 9	+4.5
21 28	1	17867.9	17868.3	−0.4
2 12	0	17832.3	17831 5	+0 8
13 21	1	17772.1	17770 0	+2.1
14 22	1	17709.1	17705 3	+3 8
5 15	0	17556 2	17557.7	+0 5
20 28	0	17481 8	17481.0	+0 8

TABLE II

Vacuum wave numbers and rotational assignments for 2-0, 1-4, 2-5 and 3-3 bands

J	2—0		1—4		2—5		3—3	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
1								
2			21263 97					22490.18
3		23637.09	63 49					89.62
4		36.52	62 92					88.97
5		35.88	62.33					88.31
6		35.16	61 74					87.49
7		34.47	61.08					86.86
8		33.71	60.44					86.06
9		32.86	59.78					85.25
10		32.00	59 00					84.35

TABLE II (contd.)

J	2—0		1—4		2—5		3—3	
	R(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)
11		31.17		58.31				83.64
12		30.22		57.54		21137 91		82.76
13		29.28		56.75		37.10		81.80
14		28.16		55.91		36.21		80.81
15		27.16		55.02		35.48		79.82
16		26.02		54.08		34.57		78.70
17		23624 89		21253.10		21133.73		22477.61
18		23.90		52 17		32.80		76.65
19		22.90		51.13		31.82		75.44
20		21.63		50.15		30.83		74.15
21		20 37		49.30		29.84		73.00
22		19.01		47.94		28.77		71.78
23	23637.09	17.63		47.03		27.75	22490.79	70.57
24	36.52	16.12		46.04		26.55	90.18	69.14
25	35.88	14 67		44.87		25.45	89.62	67 79
26	35 16	13.19		43.74		24.59	88 97	66.40
27	34.47	11.59		42.57		23.43	88.31	64.99
28	33.71	10 00		41.24		22.26	87.49	63.47
29	32.86	08.35		39.96		21.08	86.86	61.91
30	32.00	06.57	21263.97	38 67		19.69	86.06	60.71
31	31.17	04.90	63.49	37.29		18.53	85.25	59.24
32	30.22	03.13	62.92	35 95		17.25	84.35	57.63
33	23629.28	23601.39	21262.33	21234.62		21115.88	22483.64	22455.90
34	28.16	23599 54	61.74	33.18		14.63	82.76	54.28
35	27.16	97.60	61.08	31.61		13.21	81.80	52.66
36	26 02	95.72	60.44	30.23		11.83	80.81	50.89
37	24.89	93.62	59.78	28.73		10.47	79.82	49.14
38	23.60	91.65	59 00	27.17		08.86	78.70	47.28
39	22.39	89.59	58.31	25.69		07.43	77.61	45.39
40	21.03	87.52	57.54	24.00		05.88	76.65	
41	19.77	85.33	56.75	22.35		04.30	75.44	
42	18.35	83.17	55.91	20.69	21137.91	02.66	74.15	
43	16.91	80.96	55.02	18.92	37.10	01.05	73.00	
44	15.42	78.70	54.08	17.16	36.21	21099.50	71.78	
45	13.91	76.39	53.10	15.42	35.48	97.82	70.57	
46	12.36	73.96	52.17	13.58	34.57	96.11	69.14	
47	10.72	71.47	51.13	11.66	33.73	94.37	67.79	
48	09.14	68.91	50.15	10.01	32.80	92.65	66.40	
49	23607.47	23566.43	21249.30	21208.06	21131.82	21090.83	22464.99	
50	05.63	63.85	47.94	06.17	30.83	89.02	63.47	

TABLE II—(contd).

J	2—0		1—4		2—5		3—3	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
51	03.79	61.20	46.90	04 24	29.84	87.15		
52	02 10	58.49	45 64	02 22	28.77	85.23		
53	00 20	55 84	44 49	00.20	27.75	83.37		
54	23598.28	53.21	43 19	21198.11	26.55	81 54		
55	96.29	50.44	41 91	96 04	25.45	79.55		
56	94.28	47 66	40 65	93.84	24.24	77 55		
57	92.24	44.73	39 30	91 83	22.96	75.59		
58	90.09	41.80	37 93	89 62	21.66	73.45		
59	88 00	38 82	36 57	87 40	20.48	71 31		
60	85.69	35 88	35 12	85.21	19.08	69.18		
61	83 52	32 90	33.71	82 86	17.92	67.11		
62	80 96	29 75	32.17	80 58	16.36	64.94		
63	78.70	26.60	30.66	78.30	14.92	62.76		
64	76 38	23 35	29 11	75 96	13.55	60.45		
65	73 96	20.08	27.52	73.50	11.83	58 18		
66	23571 47	23516 83	21225 69	*	21110 47	21055 95		
67	68.91	13.52	24 00	*	08.86	53.56		
68	66 43	10 13	22 35	*	07.43	51 19		
69	63.85	06.76	20 69	21163 47	05.88	48.73		
70	61 20	03 24	18 92	60.93	04.30	46.34		
71	58 49		17.16	58 35	02.66	43.92		
72	55.84		15 42	55 65	01.05	41.41		
73	52.85		13 58	52 96	21099.21	38.95		
74	49.95		11.66	50 27	97.48	36.33		
75	47.08		09 68		95 51	33.65		
76	44.08		07 67		93.81	30.97		
77	41.08		05 61		91.93	28 52		
78	37.95		03.52		89.99			
79	34.94		01.48		88.08			
80	31.75		21199.32		86.08			
81	28 54		97.21		84.07			
82	25 30		94.99		82.03			
83	21.96		92 80		80.00			
84	23518.65		21190.41		21077.96			
85	15.16		88.18		75.59			
86	11.68		85.84		73.44			
87	08.18		83.50		71.31			
88	04.58		81.04		69 18			
89			78.66		66.92			
90			75.96		64.39			
91			73.50		62 06			
92			*		59 76			
93			*		57.29			
94			*		54.74			
95			63.09		52.27			
96			60.31		49 67			
97			57.55		47.14			
98			54.81		44.56			
99					41.81			

* Masked by an atomic line.

TABLE III

v' v''	Band Origin	B'_v cm^{-1}	B''_v cm^{-1}	D'_v 10^{-6} cm^{-1}	D''_v 10^{-6} cm^{-1}
2,0	23639.20	0 2082	0.2307	0.35	0.43
1,0	23269.44	0 2090	0 2307	0.35	0.43
0,0	22892.65	0.2097	0 2307	0.35	0.43
0,1	22384.67	0.2097	0.2289	0.35	0.34
0,2	21880 75	0.2097	0 2273	0.35	0.31
0,3	21382.12	0.2097	0 2262	0 35	0.23
1,4	21265 25	0 2090	0 2244	0.35	0.23
2,5	21145 28	0 2082	0 2227	0 35	0.23
3,3	22491 43	0 2073	0 2262	0.35	0.23

comparison of the upper state combination differences of (1, 0) band while in the (3, 3) band the numbering is fixed by a comparison of the lower state combination differences of (0, 3) band analysed by Rao and Rao (1962). The rotational constants of the four bands (2, 0), (1, 4), (2, 5) and (3, 3) were determined from the equation (Herzberg page 182)

$$\frac{\Delta_2 F(J)}{J+1/2} = 4B_v - 8D_v(J+1/2)^3$$

in which the combination differences of the upper and lower states are obtained from

$$\Delta_2 F'(J) = R(J) - P(J)$$

$$\Delta_2 F''(J) = R(J-1) - P(J+1)$$

by following the usual graphical procedure. The vacuum wavenumbers and the rotational assignments for the four bands are given in Table II. The J numbering of the P and R branches of 1, 4 band is shown in Plate 1(b). In determining the rotational constant of the upper state $v' = 2$, the average values of the upper state combination differences $\Delta_2 F'(J)$ for the (2, 0) and (2, 5) bands were used. The band origins, B_v and D_v values of the various upper and lower levels are collected in Table III. The values of B_e and α_e on the basis of the present work agree very well with the values reported earlier by Rao and Rao. The variation of D_v with v is too small and hence the same value of D_v is given for the levels $v'' = 4$ and 5.

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